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Preparation and Characterization of Sulfonated Polyphenylquinoxalines

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Abstract: Poly(phenylquinoxaline)s.(PPQs) are a family of aromatic condensation polymers known for their outstanding thermal and chemical stability. The pendant phenyl groups and chains isomerism improve the solubility and processing characteristics of these polymers. PPQs have also been shown to possess excellent thermo-oxidative stability and thermohydrolytic stability. This stability makes these

Figure 1 appears in color online: http://hip.sagepub.com

polymers candidates for development as proton exchange membranes (PEMs) to be used in fuel cells. In addition to thermohydrolytic stability, PEMs require high protonic conductivity and, in order to achieve this they also require high water uptake. Aromatic condensation polymers do not possess these properties, but ionomers derived from them may. The usual method to derivatiziting these polymers is through sulfonation. In the frames of the present investigation we have carried out sulfonation of two PPQs using an H_2SO_4–oleum mixture (4 : 1) as sulfonating agent at 125 °C. As a quinoxaline ring is readily formed in acidic medium synthesis of sulfonated PPQs (SPPQs) was also carried out directly from monomers using an H_2SO_4–oleum mixture as solvent, catalyst and as sulfonating agent. Depending on the conditions of the reaction (temperature, duration, and the ratio of components in a sulfonating mixture) the polymers containing 0.2–6.7% S were prepared. SPPQs are soluble in polar organic solvents; from the solutions of SPPQs high strength films (σ = 80–100 MPa) were cast. On the basis of sulfonated PPQs new cation-exchange membranes were prepared and investigated. Among the cation-exchange membranes developed those of the greatest interest are proton-exchanging membranes for fuel cells. Proton conductivity of the membranes prepared strongly depends on relative humidity and comparable with the conductivity of Nafion 117.
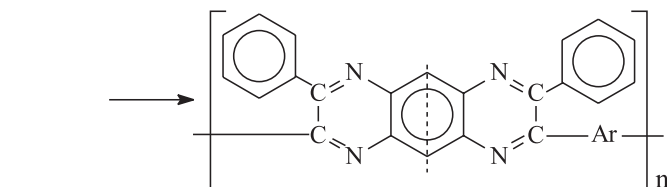
1. INTRODUCTION

Polyphenylquinoxalines (PPQs) are a family of aromatic condensation polymers known for their outstanding thermal and chemical stability [1, 2].

The most known method for the PPQs preparation is the interaction of bis(*o*-phenylenediamines) with bis(α-diketones) in protogenic solvents [1, 2] (scheme 1).
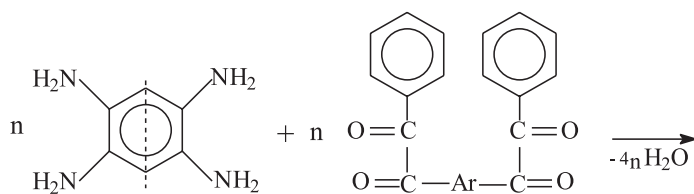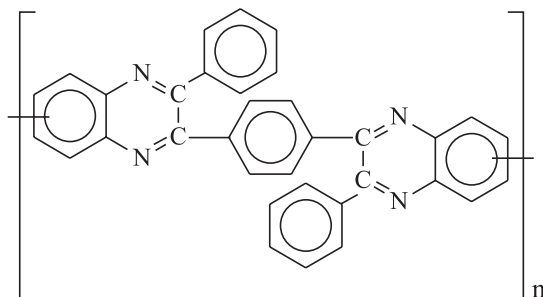

scheme (1)

The pendant phenyl groups and chains isomerism improve the solubility and processing characteristics of these polymers. These polymers have also been shown to possess excellent thermo-oxidative stability and thermohydrolytic stability [3].
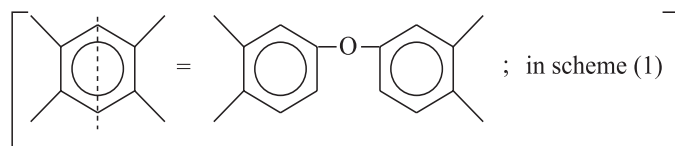
The most known PPQ commercialized in the USA and France is polymer

based on 3,3′- diaminobenzidine (DAB) and 1,4-bis(phenylglyoxalyl)benzene (BPGB).
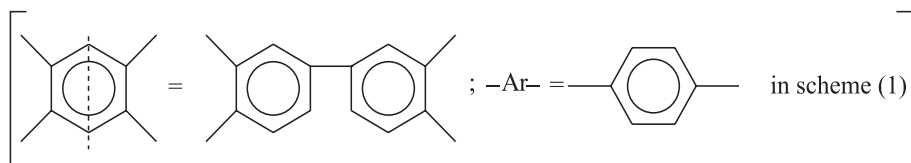

In Russia, main attention was paid to the PPQs based on 3,3′;4,4′-tetraaminodiphenyl ether (TADE)

This monomer, which was firstly described by Stille et al. [4] and commercialized on a pilot scale in Russia, is more nucleophilic and less toxic when compared with DAB. In addition, incorporation of the ether groups in the PPQs macromolecules leads to the improved flexibility of the target polymers.

4,4′-bis(phenylglyoxalyl)diphenyl ether (BPGDPE) and especially BPGB were used As comonomers of TADE [5].
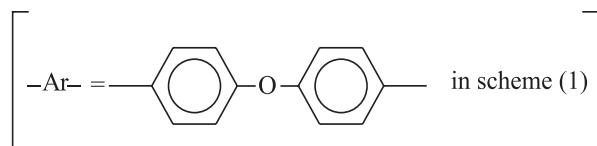
A very simple and inexpensive route for the preparation of BPGB is based on the interaction of terephthalic acid dichloride with a two-fold molar amount of styrene with subsequent oxidation of the 1,4-distyrylbenzene thus formed (scheme 2) [6, 7].

scheme 2
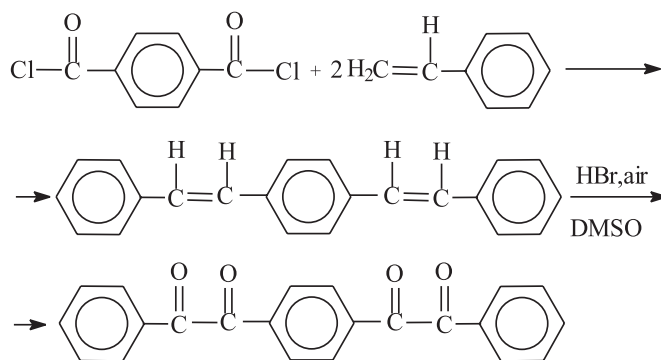
PPQs of general formula
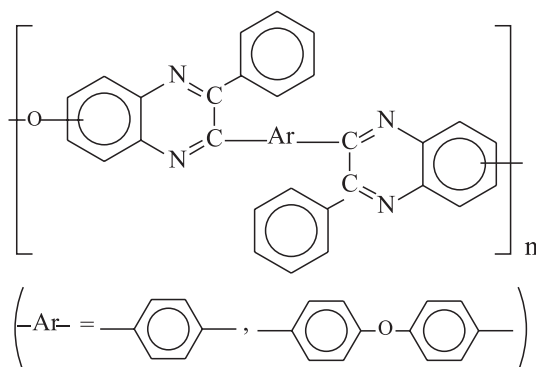
are soluble in CHCl$_3$, *m*-cresol and benzyl alcohol. They demonstrate good film-forming properties, moderate glass transition temperatures (250–280 °C), excellent thermo-oxidative and thermohydrolytic stability.

This stability makes these polymers candidates for development as proton exchange membranes (PEMs) to be used in fuel cells [8, 9].

In addition to thermohydrolytic stability, PEMs require high protonic conductivity and in order to achieve this they also require high water uptake. Aromatic condensation polymers do not possess these properties, but ionomers derived from them may. The usual method to derivatiziting these polymers is through sulfonation [8, 9].

2. EXPERIMENTAL PART

2.1. *Monomers*

TADE was prepared and purified in accordance with [4]. Yield 80%. M.p. 149–150 °C; lit. m.p. 150–151 °C [4].

BPGB was prepared and purified in accordance with [6, 7]. Yield 54%. M.p. 125–126 °C; lit. m.p. 125–126 °C [10].

BPGDPE was prepared and purified in accordance with [5]. Yield 74%. M.p. 106–107 °C; lit. m.p. 106.4–107.4 °C.

2.2. Preparation of PPQs

To a stirred slurry of TADE (23 g, 0.1 mol) in m-cresol (200 mL), 0.1 mol of bis-(α-diketone) as powder was added over a period of 5 min. Additional solvent (50 mL) was used to wash in the residual bis-(α-diketone) and the reaction temperature was maintained at 35 °C by cooling in a water bath. The reaction mixture was stirred at ambient temperature for 18 h to yield a viscous solution that was poured into methanol in a Waring Blender to yield a fibrous cream-colored polymer which, after washing with hot methanol and drying at 130 °C in vacuo, exhibited the properties listed in table 1 (samples 1 and 9).

2.3. Sulfonation of PPQs

PPQ (15 g) and a sulfuric acid–oleum (4 : 1) mixture (200 mL) were placed in a three-necked flask equipped with a stirrer. The reaction mixture was stirred at room temperature for 20 h until the polymer was completely dissolved. Then, the solution was heated at 125 °C for 20 h. The viscous solution of the polymer was cooled and poured into a tenfold excess of distilled water. The precipitate of the polymer was filtered, thoroughly washed with water until a neutral reaction was reached, then washed with alcohol and dried in vacuo at 100 °C for 20 h. The properties of the polymers are summarized in the table 1.
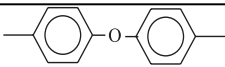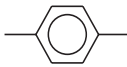
2.4. Synthesis of PPQs with simultaneous sulfonation

TADE (2.3 g, 0.01 mol), BPGB (3.74 g, 0.01 mol) and the sulfuric acid–oleum mixture (25 mL) were placed in a three-necked flask equipped with a stirrer and an inlet for argon. The reaction mixture was heated at 125 °C for 25 h in a flow of argon. The reaction mixture was then cooled and poured into a tenfold excess of distilled water. The formed precipitate was filtered off, washed with water until the reaction was neutral and then with ethanol. The polymer was dried in a vacuum at 130 °C for 20 h. η_{red} (0.5% solution of polymer in N-methyl-2-pyrrolidone at 25 °C) 0.8 dL g^{-1}.

2.5. Methods of measurement

For electroconductivity measurement of the membranes in solutions of various salts (0.1 mol L^{-1}), we used a thermostated cell with a mobile electrode. The membrane resistance was calculated using the equation $R = d/[(R_m - R_s)S]$, where R_m and R_s are the resistances (Ω cm) of the membranes in solutions and the solutions, respectively, at a

Table 1. Some characteristics of sulfonated poly(phenylquinoxaline)s and the conditions of their preparation.

Sample	–Ar–	Reaction temperature (°C)	Reaction time (h)	Sulfur content (wt.%)	$T_{softening}$* (°C)	Properties of films upon stretching		The Brinell hardness H_B (kg cm^{-2})
						σ (MPa)	ε (%)	
1		25	25	–	250/250	100	98	20
2	"	50	10	–	250/250	105	85	
3	"	80	10	0.2	260/275			
4	"	100	5	0.1	250/260			
5	"	100	10	1.1	285/340			
6	"	125	20	3.35	325/–	92	69	25
7	"	125	30	4.65	340/–			
8	"	125	40	6.75	360/–	81	14	25
9		50	20	–	280/280	110	120	
10	"	100	10	1.2	315/360			
11	"	125	20	3.4	355/–			

*The softening temperatures of sulfonated PPQs are given in the numerator and the softening temperatures of these polymers heated at 320–360 °C for 1 h in a flow of argon are given in the denominator.

frequency of 10^3 Hz; S is the membrane surface (cm^2); and d is the membrane thickness (cm).

The transport number for cation through the membrane ($\bar{t}_+$) was determined by means of the emf technique using a 0.01 mol L^{-1} concentration of salt in water on one side of the membrane and 2.0 mol L^{-1} on other side.

Water absorption (Q) was calculated with the weight measurements by the relation

$$Q = \frac{P_w - P_d}{P_d} \times 100$$

where P_w and P_d are weights of the film that was swollen in water to equilibrium and the dry film, respectively. The data on membrane water absorption were used to calculate the number of water molecules per one monomer unit of the polymer (N).

3. RESULTS AND DISCUSSION

Within the present investigation we carried out sulfonation of two PPQs using an H$_2$SO$_4$–oleum mixture (4 : 1) as the sulfonating agent at 125 °C [11, 12] (scheme 3) (Sulfonation of different PPQs has also been carried out using chlorosulfonic acid as sulfonating agent [12–14]).
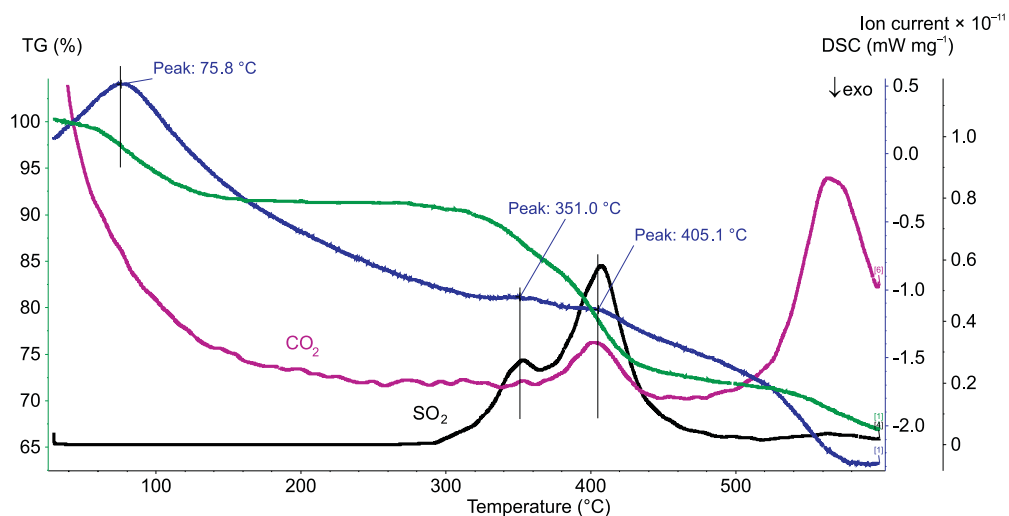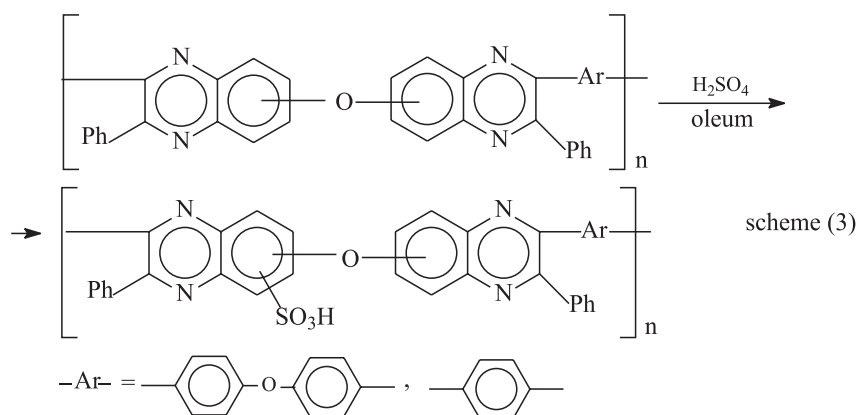
Figure 1. Results of sulfonated polyphenylquinoxaline differential scanning calorimetry.


scheme (3)

Sulfonation of the PPQs based on TADE proceeded more easily than the sulfonation of the PPQs based on DAB.

Depending on the reaction conditions (temperature, duration and the ratio of components in a sulfonating mixture) polymers containing 0.2–6.7% S were prepared (table 1).

The IR spectra of sulfonated PPQs (SPPQs) showed an absorption band at 650 cm^{-1}, which is characteristics of the stretching vibrations of the SO_3H group [15].

According to thermogravimetric analysis (TGA), the weight loss of SPPQ upon heating in air at 450 °C (after the evolution of water) was 15–17%. According to differential scanning calorimetry (DSC) of the sulfonated PPQ (sample 8 in table 1), the membrane desorbed water at temperatures below 100 °C; at temperatures above 300 °C a desulfonation reaction took place (figure 1).

Depending on the extent of sulfonation, the softening temperature was in the range 250–350 °C (table 1); that is, in some cases the softening temperature increased by 100 °C in comparison with the starting PPQ [16]. After thermal treatment at 320–360 °C for 1 h in a flow of argon, the SPPQs became insoluble. Their IR spectra showed the disappearance of the band at 650 cm^{-1}, and the appearance of a band at 1130 cm^{-1}, which is characteristic of the stretching vibrations of the SO$_2$ groups [15]. It is probable that under these conditions, intermolecular interaction took place. This agrees well with the data of Polyanskii and Tulupov [17]

scheme (4)
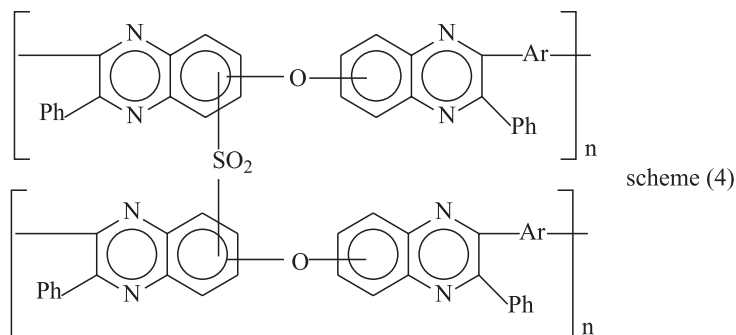
In addition to the formation of the sulfone bridge, desulfonation to form the Ar–Ar bond is possible [17]. The SPPQs were soluble in *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, *N,N*-dimethylacetamide and benzyl alcohol, but they were insoluble in chloroform, as is characteristic of PPQs [16]. High-strength films (σ = 80–105 MPa) were obtained from solutions of polymers.

It is known that the quinoxaline ring was readily formed in acidic medium [18, 19]. Therefore, it was advisable to synthesize SPPQs directly from monomers. This naturally simplifies the technology of their synthesis, and sulfuric acid/oleum acts as a solvent, catalyst, and sulfonating agent at the same time.

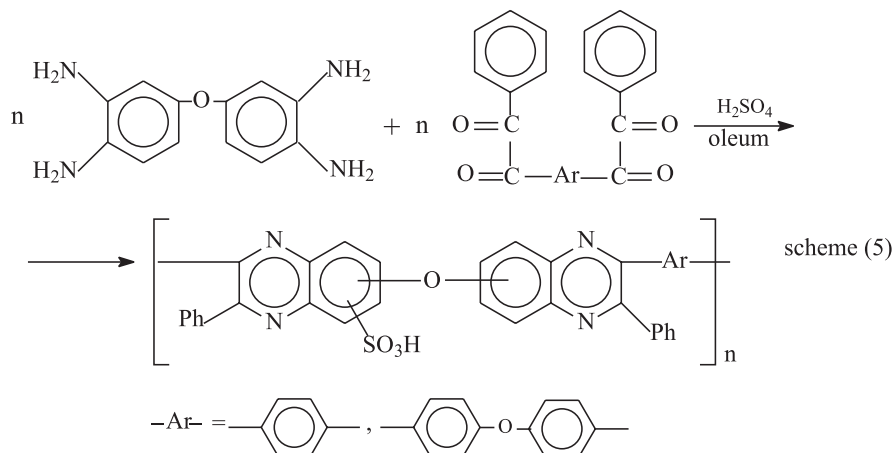The preparation of the polymers is represented by scheme 5.

scheme (5)

Table 2. Characteristics of SPPQs.

Number of specimen	Sulfur content (wt.%)	Number of sulfonate groups per a monomer unit of the polymer, α	SEC (mg-equiv g^{-1})
1	2.05	0.37	0.62
2	2.57	0.58	0.93
3	3.65	0.72	1.15
4	4.50	0.90	1.40
5	5.57	1.15	1.75
6	6.10	1.27	1.90

No SPPQ was formed in sulfuric acid at room temperature for 40 h. When the temperature was increased to 50, 100, and 125 °C, sulfonation of PPQ took place, although the content of sulfur was small and viscosity characteristics were low: S, 0.7% and η_{red} = 0.08 dL g^{-1}; S, 0.8% and η_{red} = 0.25 dL g^{-1}; S, 1.1% and η_{red} = 0.3 dL g^{-1}, respectively. The addition of oleum to sulfuric acid 20 h after the beginning of the reaction had almost no effect on the viscosity of the polymer and the extent of its sulfonation. Only polyheterocyclization carried out at 125 °C for 25 h using a sulfuric acid–oleum (4 : 1) mixture as a solvent, catalyst, and sulfonating agent yielded high-molecular-weight polymers (η_{red} = 0.5–0.8 dL g^{-1}) containing from 2 to 4.2% S.

The IR spectra of sulfonated PPQs did not show the absorption bands at 1680 cm^{-1} and in the region 3200–3400 cm^{-1} which are characteristic of the stretching vibrations of the carbonyl groups of the starting tetraketones and amino groups of the starting tetraamines, respectively; the absorption bands at 650 cm^{-1}, which are characteristic of the stretching vibrations of SO$_3$H groups [16], were observed in these spectra. According to TGA, as in the case of polymers prepared by the first method, the weight loss upon heating in air of SPPQs prepared directly from the monomers was 5–7% at 450 °C. Depending on the extent of sulfonation, the softening temperature increased by 40–70 °C, in comparison with nonmodified PPQs [16]. The polymers were soluble in amide solvents. This made it possible to prepare high-strength films from these polymers (ε = 20–30%, σ = 70–80 MPa).

The study of hydrolytic stability in an autoclave showed that the films retain mechanical properties at 250 °C and a pressure of water vapors of 40 atm during 600 h.

The electrochemical properties of SPPQ films were investigated for the samples with sulfur content 2.05–6.10 wt.%; e.g. number of sulfonate groups per monomer unit of the polymer (α) 0.37–1.27 (table 2) [20–22].

A change in the concentration of sulfonate-containing units in the chain and the related statistical exchange capacity (SEC) of films significantly affected the specific electroconductivity (κ) of these membranes. For the films with an SEC of 0.6 and 1.9 mg-equiv g^{-1}, the κ value is 10^{-5} and 10^{-2} Ω^{-1} cm^{-1}, respectively (figure 2).

The data presented in figure 1 also indicate some selectivity of univalent cation transport under the current passing in the series ($K_{Na}^+ > K_K^+ > K_{Cs}^+ > K_{Li}^+$) for the films prepared from SPPQ with a high content of sulfonate groups (SEC is 1.1 to 1.9 mg-
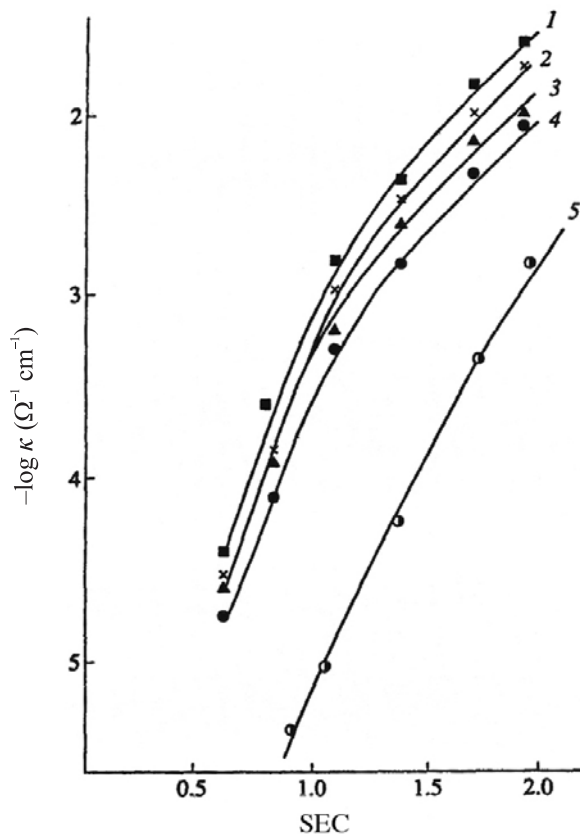
Figure 2. Specific conductivity of membranes with various ionic forms: (1) Na$^+$, (2) K$^+$, (3) Cs$^+$, (4) Li$^+$ and (5) Ca^{2+} as a function of SEC of the membranes.

equiv g^{-1}). The feature is not characteristic of commercial membranes with high conductivity (for example, a KM-40 membrane has t$_+$ = 0.7–0.75 and κ = 10–3 × 10^{-3} Ω^{-1} cm^{-1}) [23].

The transport selectivity virtually disappeared for the films prepared from SPPQs with a low content of SO$_3$– groups (SEC is 0.6 to 1.1 mg-equiv g^{-1}). A knee was observed in the log κ versus SEC curves for the membranes from polymers with SEC of 1.0 to 1.1 mg-equiv g^{-1}.

A significant decrease in electroconductivity was observed for films in the Ca^{2+} form with respect to films in the Na$^+$ form. The excess in specific conductivity of films in the Na$^+$ form with respect to the Ca^{2+} form was two orders of magnitude (SEC was 0.6 to 1.4 mg-equiv g^{-1}). Addition of Ca^{2+} to the polymer resulted in a strong interaction between these cations and the sulfonate groups of various macromolecular chains. This interaction reduced the distance between macrochains and withdrew water molecules from
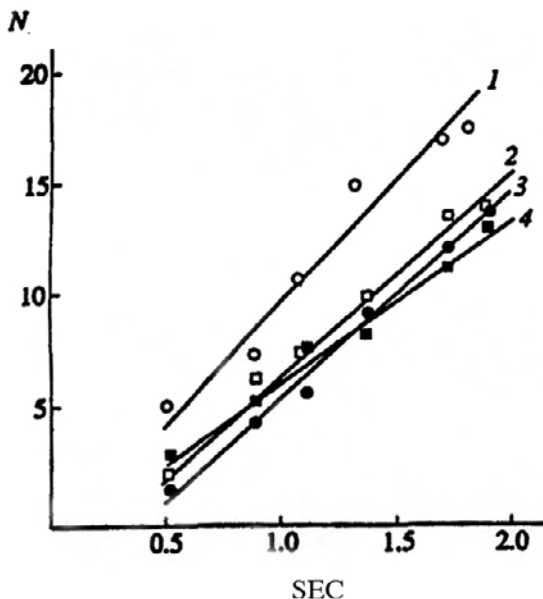
Figure 3. Number of water molecules per one monomer unit of the polymer in uniformly swollen membranes ionic forms: (1) Na^+, (2) Li^+. (3) Cs^+ and (4) Ca^{2+} against SEC of the membranes.

the environment of the polar groups. It was this interaction and reduction in the number of water molecules that seemed to account for a sharp increase in the resistance of the films in the Ca^{2+} form.

Important information was obtained from a comparative analysis of data on water content in the films (figure 3) and selective transport for the cations with respect to anions (figure 4).

Water absorption (Q) was calculated with the weight measurements by the relation

$$Q = \frac{P_w - P_d}{P_d} \times 100$$

where P_w and P_d are weights of the film that was swollen in water to equilibrium and the dry film, respectively. The data on membrane water absorption were used to calculate the number of water molecules per one monomer unit of the polymer (N).

The data presented in figure 3 indicate a significant increase in the transport number t_+, from 0.75 to 0.95, within the SEC range of 2.0 to 1.2 mg-equiv g^{-1}.

In other words, the membranes prepared from polymers with an SEC within this range had a low selectivity of cation transport with respect to that of the anion. The SPPQ membranes with an SEC below 1.2 mg-equiv g^{-1} were characterized by enhanced selectivity and identical $\bar{t}_+$ values (0.95 to 0.99) for various ionic forms (figure 4).
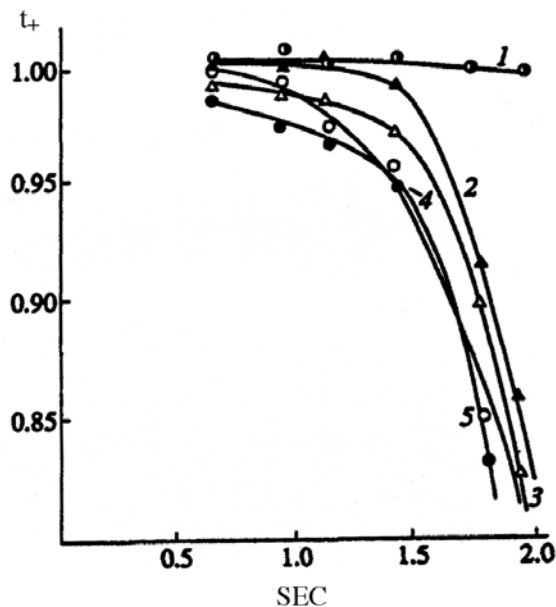
Figure 4. Transport number of cations : (1) Ca^{2+}, (2) Li^+, (3) Na^+, (4) K^+, and (5) Cs^+ against SEC of the membranes.

The proton conductivity of PPQs was determined at room temperature (20 °C). Proton conductivity was assured by the coulombic efficiency measurements made by comparing the hydrogen evolved in an electrolytic cell to the measured current. The use of non-conjugated linking groups, such as –O–, between the phenyl rings discouraged electron injection into the solid electrolyte.

Attempts to rationalize the conductivity of PPQs can be done by comparing their water uptake and their acid content. The equivalent weight is frequently used to compare relative acid content of the polymers, but a more precise way of looking at this factor is from the perspective of the density of the sulfonic acid groups in the water swollen membrane. This value, ρ SO_3H has units of meq cm^{-3}, which can be calculated from the sulfonation level, the dry weight, and the wet volume [24].

Comparison of conductivity between various SPPQs did not correlate with either acid density or water uptake. The conductivity of SPPQ 6 containing 1.27 sulfonate groups per monomer unit of the polymer (table 2) was 9.7×10^{-3} s cm^{-1}, which was comparable with the conductivity of Nafion 117 [25].

The dependence of protonic conductivity on relative humidity for SPPQs-11 (table 1) is shown in figure 5.

The results indicate that protonic conductivity increased significantly with increasing relative humidity.
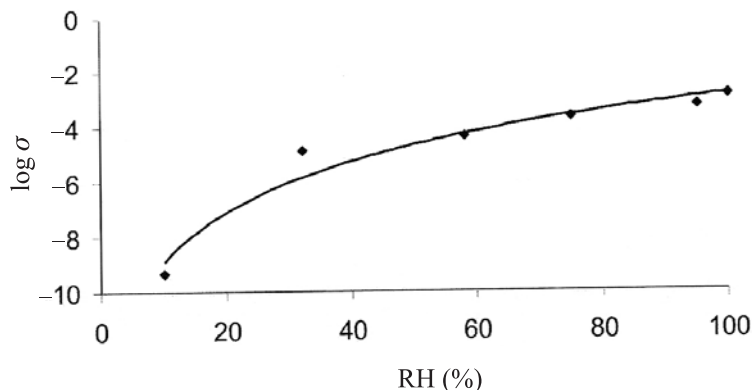
Figure 5. Dependence of protonic conductivity of SPPQ-11 on relative humidity.

It is known that, at the same SEC values, the cation-exchange membranes prepared from sulfonate-containing aromatic polyamides are characterized by high selectivity ($\bar{t}_{Na^+}$ is 0.96 to 0.98) and contain a small number of water molecules ($N = 4$ or 5) [26]. Essentially, these materials achieve a uniform distribution of H_2O molecules in the matrix and, correspondingly, in the channels [27].

Comparing the electrochemical parameters and the data on water capacity for the membranes prepared from SPPQs and polyamides, we can draw a conclusion about significant differences in the structure of channels, i.e., the pathways for electrotransport of ions through the membrane. The drying of sulfonate-containing polyphenylquinoxalines that include bulky groups (heterocycles and benzene rings) forms the channels, which combine wide sections with high content of ionogenic groups and more compact narrow sections with low content of SO_3 groups. The former and the latter sections contain different number of molecules and produce internal heterogeneity in the distribution of water molecules over the total length of the electroconducting pathways.

Apparently, it is the narrow sections of the channels, which contain around four or five water molecules which determine the high cationic selectivity and prevent the non-exchange-absorbed electrolyte from penetration into a channel in the films with SEC below 1.2 mg-equiv g^{-1}.

The wide sections in the flow channel containing up to 20 water molecules per monomer unit (SEC is above 1.2 mg-equiv g^{-1}) only slightly affect the selectivity of transport of cations with various sizes (figures 2 and 4). Meanwhile, their presence ensures high specific conductivity of films with high SEC values.

The channels in sulfonate-containing polyamides [26] are formed in such a way that the water molecules are distributed more or less uniformly over the channel length. The selectivity for ions with various sizes appears if the water content is less than four to five molecules per monomer unit.

Thus, the study of electrochemical behavior of the membranes prepared from new PPQ with sulfonate groups enabled us to assume the structure of the channel length as a combination of wide and narrow sections differently occupied by ionogenic groups and water molecules connected therein due to internal heterogenity of the material.

NOTE

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